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Spontaneous Formation and Stability of Surfactant Vesicles

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1 Introduction

Vesicles are bilayer shells enclosing a pool of solvent. They are generally metastable structures where thermodynamic equilibrium corresponds to a lamellar phase, possibly coexisting with excess solvent. The problem of thermodynamic equilibrium can be a difficult issue to reveal experimentally, a vesicle preparation may remain stationary for long periods of time. Nonionic ethylene oxide based surfactants make useful model systems of surfactant self-assembly because the monolayer spontaneous curvature, H_0 , varies strongly with the temperature. At lower temperatures, the surfactant monolayer film prefers to curve away from water ($H_0 > 0$) and forms normal micelles in water. At higher temperatures H_0 is negative and the surfactant film has a preference for curving towards water. Bilayer structures form typically when H_0 is near zero. Here we will discuss the stability of nonionic vesicles and how they can be formed spontaneously when rapidly heating a micellar solution. Experiments also show that the vesicle bilayer can be perforated, where the holes open and close spontaneously as the temperature and thus H_0 is varied.

2 Vesicle Ripening

Precipitated dispersions and emulsion often undergo coarsening by Ostwald ripening, where small particles dissolve and large particles grow, driven by the interfacial free energy. At a first glance one would expect an unstable vesicle dispersion to evolve in a similar way, lowering the curvature free energy. However, to leading order the curvature free energy is independent vesicle size, being $8\pi\kappa'$ per vesicle where κ' is the spherical bilayer bending modulus. In this case the molecular exchange between vesicles are purely random events. A vesicle ripening process thus has to be driven by higher order terms of the curvature energy. The next term is also expected to be positive, increasing the penalty for high curvatures. With such a term included, it turns out that there is a net flow of molecules from large to small

vesicles making a broad size distribution more narrow. Such a system will thus get trapped in a metastable state if the number of vesicles remain unchanged.[1]

3 Vesicle formation

With nonionic surfactants we can rapidly heat a micellar solution to a temperature, where the spontaneous curvature is near zero. The micelles fuse and grow into larger aggregates that eventually form a bilayer that spontaneously close into a vesicle, due to the unfavorable line energy at the edge of a bilayer disc that increases with increasing disc size. Since the vesicle energy is (to leading order) size independent it follows that discs should spontaneously close into vesicles when exceeding a certain size. This occurs at vesicle radius of $R^*=2\kappa'/\lambda$, where λ is the line tension. For the nonionic surfactant $R^*\approx 10$ nm. To observe this, would require very rapid heating. In practice the resulting vesicle size is rather determined by micelle aggregation kinetics. [2]

4 Perforated Vesicles

Mesh-like or perforated lamellae have been reported for several systems and seem to occur as precursors before a lamellar to cubic phase transition. [3-5] Dilute nonionic vesicles also appear to be perforated and show ion permeability that strongly depends on the temperature. Perforation increases when H_0 is increased (temperature decreased). The situation is reversible with respect to temperature cycles. Hence, holes may be opened or closed by simply varying the temperature.

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